

**IN THE UNITED STATES PATENT
AND TRADEMARK OFFICE**

Applicant(s): Shinji Tsuchikawa et al
Serial No.: 10/511,102
Filed: October 14, 2004
For: THERMOSETTING RESIN COMPOSITION, AND PREPREG
AND LAMINATED BOARD USING THE SAME
Art Unit: 1713
Examiner: Ives Wu

Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

DECLARATION UNDER 37 CFR 1.132

SIR:

I, Shinji Tsuchikawa, an inventor of this case,
declare and say as follows.

I am one of the joint inventors of the present U.S.
Patent Application as identified above and understand the
English language. I studied the Official Action dated
August 11, 2005 received in said application.

In order to clarify that the present invention is not
obvious over combination of the inventions of Tsuchikawa et
al. (U.S. Patent No. 6,671,017) and Ernst et al. (U.S.
Patent No. 3,046,231) and Kawase et al. (U.S. Patent No.
3,953,539), I have conducted comparative experiments as

mentioned below under my supervision.

II. Comparative experiments

In the following Examples, all part(s) mean part(s) by weight unless otherwise specifically mentioned.

Resin of Component (2): (2-1) Copolymer resin comprising styrene and maleic anhydride (trade name: Dylark D-332; produced by Dylark Co., weight average molecular weight: 150,000, copolymerization composition ratio: a ratio between m and n in formula (II) and formula (III) is $m/n=7$)

A thermosetting nitrogen atom-containing resin as Component (3): (3-2) Triallyl isocyanurate

Epoxy resin of Component (4):

(4-1) Biphenyl type epoxy resin (Epoxy equivalent: 193)

Curing catalyst or curing accelerator:

TEA: Triethylamine

ZnNph: zinc naphthenate

P-25B: 2,5-dimethyl-2,5-di(t-butylpentyloxy)-3-hexen-3PCP
para-cumylphenol

2PZ: 2-phenyl imidazole

Flame retardant (Comparative example):

D: Methylphosphinic acid

E: Diethylphosphinic acid

F: Triphenylphosphine

G: Triphenylphosphite

Synthetic example 1:

Component (3): Preparation of cyanate ester resin (3-1)

Into a 3L-volume reactor equipped with a thermometer, a stirrer, and a condenser and being capable of heating and cooling were charged 1,519 g of 2,2-di(cyanatophenyl)-

propane, 23.1 g of para-cumylphenol, and 1,022 g of toluene. The mixture was heated to 80°C, and 0.22 g of an 8% by weight solution of zinc naphthenate was added thereto while maintaining the temperature at 77 to 83°C. After completion of the addition of the solution, a reaction was performed at 80°C for 3.5 hours to obtain cyanate ester resin solution (3-1).

The solid content of the solution (3-1) was 61% by weight, and a measurement using gel permeation chromatography confirmed that 45 mol% of 2,2-di(cyanatophenyl)propane as the raw material formed a trimer and/or a larger polymer by self-polymerization.

Synthetic Example 2

Components (2-1) and (3): (A-1) Preparation of Semi-IPN (interpenetrating polymer network) structure between a copolymer resin comprising styrene and maleic anhydride, and a cyanate ester resin

Into a 5L-volume reactor equipped with a thermometer, a stirrer, and a condenser and being capable of heating and cooling were charged 1,519 g of 2,2-di(cyanatophenyl)propane, 23.1 g of para-cumylphenol, 1,519 g of a copolymer resin comprising styrene and maleic anhydride (trade name: Dylark D-332, produced by Dylark), and 1,022 g of toluene. The mixture was heated to 100°C and dissolved. After dissolution, 0.88 g of an 8% by weight solution of zinc naphthenate was added to the resultant solution while maintaining the temperature at 97 to 103°C. After completion of the addition of the solution, a reaction was performed at 120°C for 5 hours to obtain solution (A-1) containing a semi-IPN (interpenetrating polymer network) structure between the copolymer resin comprising styrene and maleic anhydride, and a trimer and/or a larger polymer having a triazine ring derived from the cyanate ester resin. The solid content of the solution (A-1) was 67% by weight, and a measurement using gel permeation chromato-

graphy confirmed that 60% by mol of 2,2-di(cyanatephenyl)-propane as the raw material formed a trimer and/or a larger polymer by self-polymerization. A copolymerization composition ratio between styrene and maleic anhydride was such that a ratio between m and n in formula (II) and formula (III) was $m/n=7.0$.

Comparative examples 7 to 10

The above-mentioned flame retardant (D, E, F or G); Copolymer resin comprising styrene and maleic anhydride (2-1) which is Component (2); Cyanate ester resin (3-1) obtained in Synthetic example 1 which is Component (3); Semi-IPN structure polymer (A-1) comprising Component (2) obtained in Synthetic example 2 and Cyanate ester resin which is Component (3); Epoxy resin (4-1) which is Component (4); and further, triethylamine, zinc naphthenate, 2,5-dimethyl-2,5-di(t-butylperoxy)-3-hexen-3, and para-cumylphenol as curing catalyst or curing accelerator, were mixed in formulation ratio (parts by weight) shown in Table 1 to obtain uniform varnishes.

The obtained varnishes were each formed to substrates for evaluation of resin sheets and copper-clad laminated boards according to the following method, and the properties thereof were evaluated, respectively. The results are shown in Table 1.

(a) Resin sheet

The obtained varnishes were individually applied onto a PET film, and dried by heating at 160°C for 10 minutes and the solids were taken out by a cast method. Then, the solids taken out were pressed at a pressure of 25 kg/cm² at a temperature of 185°C for 90 minutes to obtain resin sheets.

Using the thus obtained resin sheets, a dielectric constant (1 GHz) and a dielectric dissipation factor (1 GHz) were measured according to the following methods.

(b) Copper-clad laminated board

E-glass cloth having a thickness of 0.1 mm was impregnated and coated with each of the varnishes and dried by heating at 160°C for 10 minutes to obtain a prepreg having a resin-content of 55% by weight.

Then, four pieces of prepregs were laminated, 18 μm electrolytic copper foils were disposed on the upper and bottom surfaces of the prepregs and pressed at a pressure of 25 kg/cm² at a temperature of 185°C for 90 minutes to obtain a copper-clad laminated board.

Then, the obtained copper-clad laminated boards were immersed in a copper etching solution to remove the copper foils to obtain substrates for evaluation.

Using the thus obtained substrates for evaluation of the copper-clad laminated boards, a dielectric constant (1 GHz), a dielectric dissipation factor (1 GHz), moisture absorption (water absorption), resistance to soldering heat, adhesion (peel strength), and a glass transition temperature were measured or evaluated according to the following methods.

(1) Measurement Method of Dielectric Constant and Dielectric Dissipation Factor

A dielectric constant and a dielectric dissipation factor of each of the obtained substrates for evaluation of the resin sheets and the copper-clad laminated boards were measured at a frequency of 1 GHz using a dielectric constant measurement apparatus (product name: HP4291B), produced by Hewlett-Packard Company.

(2) Measurement of Glass Transition Temperature

Evaluation was performed by observing thermal expansion properties of each of the obtained substrates for evaluation of the copper-clad laminated boards using a TMA test apparatus.

(3) Evaluation of Flame Retardancy

From the substrates for evaluation obtained by immersing the copper-clad laminated boards in a copper etching solution to remove the copper foils, test pieces cut out to a length of 127 mm and a width of 12.7 mm were produced. Then, flame retardancy of each test piece was evaluated according to the test method (V method) of UL-94.

(4) Evaluation of Resistance to Soldering Heat

The copper-clad laminated boards were immersed in a copper etching solution to remove the copper foils to produce evaluation substrates. Each of the obtained substrates for evaluation was immersed in a solder bath at a temperature of 288°C for 20 seconds. Then, resistance to soldering heat of each substrate for evaluation was measured by observing the appearance of each substrate.

(5) Evaluation of Moisture Absorption (Water Absorption)

The copper-clad laminated boards were immersed in a copper etching solution to remove the copper foils to produce substrates for evaluation. Each of the obtained substrates for evaluation was subjected to pressure cooker treatment at 121°C at 2 atm. for 4 hours using a pressure cooker test machine, produced by Hirayama Corporation. Then, water absorption of each substrate for evaluation was measured.

(6) Evaluation of Adhesion (Peel Strength)

The copper-clad laminated boards were immersed in a copper etching solution to form thereon copper foils with a width of 1 cm to produce evaluation substrates. Then, peel strength of each substrate for evaluation was measured using a rheometer.

Table 1

Items			Compara- tive example 7	Compara- tive example 8	Compara- tive example 9	Compara- tive example 10
Formulation amount [part(s)]	Phosphor type Flame retardant	D	62.4			
		E		62.4		
		F			62.4	
		G				62.4
	Component (2)	2-1	50.0	50.0	50.0	50.0
	Component (3)	3-1	100.0	100.0	100.0	100.0
	Component (4)	4-1	47.2	47.2	47.2	47.2
	Curing catalyst	TEA* ⁴	0.1	0.1	0.1	0.1
		ZnNph* ⁵	0.1	0.1	0.1	0.1
		PCP* ⁶	10.7	10.7	10.7	10.7
Evaluation results	Dielectric constant	a: Resin sheet	3.4	3.5	3.3	3.3
		b: Lami- nated board	3.9	4.0	3.8	3.9
	Dielectric dissipation factor	a: Resin sheet	0.009	0.008	0.008	0.009
		b: Lami- nated board	0.013	0.012	0.012	0.013
	Flame retardancy		inflammation	inflammation	inflammation	inflammation
	Moisture absorption [%by weight]		1.3	1.2	1.3	1.2
	Resistance to soldering heat		Swollen	Swollen	Swollen	Swollen
	Peel strength [kN/m]		0.2	0.2	0.2	0.2
	Glass transition temperature [°C]		100	78	80	95

As can be clearly seen from Table 1, the resin compositions of Comparative examples do not have properties possessed by the compositions of the present invention, and show poor flame retardancy, heat resistance, moisture resistance and adhesiveness to a copper foil.

III. Conclusion

I believe that the above results would be indeed surprising and could never be expected from the combination of the descriptions of Tsuchikawa et al. and Ernst et al. and Kawase et al. Thus, I do not believe that the present invention is obvious over the references in combination cited by the Examiner.

IV. I further declare that all statements made herein of my own knowledge are true and that all statements made in information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001, of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: Feb. 16 / 2006 Shinji Tsuchikawa